



Short communication

Wetting of sodium on β'' -Al₂O₃/YSZ composites for low temperature planar sodium-metal halide batteries

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H I G H L I G H T S

- Thin films of Sn at the surface of β'' -Al₂O₃ samples was shown to improve the wetting of Na.
- Wetting was further improved by removing surface water at high temperature under vacuum.
- Complete wetting of Na on the β'' -Al₂O₃ surface was achieved at temperatures as low as 200 °C.
- Electrical conductivity and activation energies were in good agreement with the literature.
- Ability to use low cost polymeric seals to be used at operating temperatures of ≤ 200 °C is realized.

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A B S T R A C T

Wetting of Na on β'' -Al₂O₃/YSZ composites was investigated using the sessile drop technique. The effects of moisture and surface preparation were studied at low temperatures. Electrical conductivity of Na/ β'' -Al₂O₃-YSZ/Na cells was also investigated at low temperatures and correlated to the wetting behavior. The use of planar β'' -Al₂O₃ substrates at low temperature with low cost polymeric seals is realized due to improved wetting at low temperature and conductivity values consistent with the literature.

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1. Introduction

Rechargeable high temperature battery technologies based on the molten Na anode and the β'' -Al₂O₃ solid electrolyte (BASE) offer potential solutions for large scale electrical energy storage applications. There are two primary battery technologies based on liquid Na as the negative electrode and β'' -Al₂O₃ as the electrolyte, namely, sodium–sulfur and sodium–metal halide.

The sodium–sulfur (Na/S) battery was pioneered at Ford in the late 1960s for electric vehicle applications [1] and more recently further developed by the Tokyo Electric Power Company in collaboration with NGK Insulator for utility energy storage [2]. Na/S batteries are characterized as having a high efficiency of charge/

discharge (~90%), high energy density, and long cycle life. However, Na/S batteries are operated at high temperatures ~350 °C, have a highly corrosive discharge product, sodium polysulfide, and more susceptible to burn if fracture occurs across the electrolyte.

The sodium–metal halide battery is often referred to as the ZEBRA cell and was developed in the mid 1980 [3] in South Africa. The sodium–metal halide battery also utilizes liquid Na and a β'' -Al₂O₃ electrolyte but also includes a secondary electrolyte in the positive electrode and an insoluble metal halide as the positive electrode. The sodium–metal halide batteries are characterized as having a higher operating voltage, a broader operating temperature regime, are less corrosive, and have safer reaction products.

Recent results at the Pacific Northwest National Laboratory (PNNL) have shown that sodium-metal halides cells are capable of operating at temperature below 200 °C with good stability [4]. These studies utilized a sodium nickel chloride battery with

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Table 1
Surface preparation techniques used in wetting studies and conductivity measurements.

Technique #	Preparation conditions
1	Control – sample used after sintering and stored in mylar bags in a glove box.
2	Sample heated to 300 °C in vacuum (10^{-6} atm), cooled, and immediately transferred to mylar bags and stored in a glove box.
3	Samples sputtered with Sn under vacuum (10^{-6} atm and ~ 0.5 μm thick), and immediately transferred to mylar bags and stored in a glove box.
4	Sample heated to 300 °C in vacuum (10^{-6} atm), cooled under vacuum, sputtered with Sn (~ 0.5 μm thick), and immediately transferred to mylar bags and stored in a glove box.

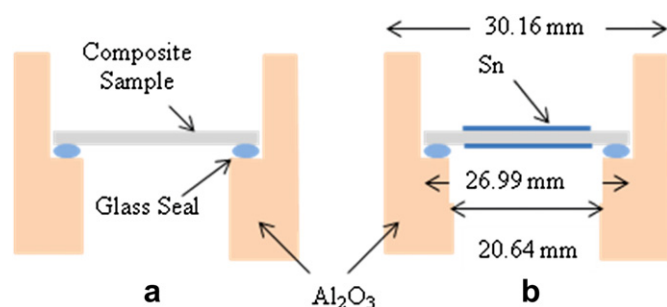


Fig. 1. Sample preparation and dimensions for conductivity measurements (a) sealing composite sample into Al_2O_3 holders and (b) surface treatment.

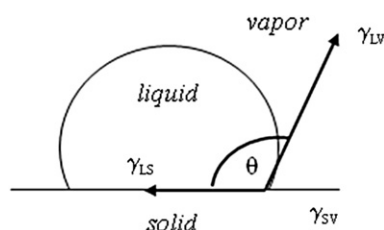


Fig. 2. A schematic diagram of the sessile drop techniques showing the contact angle θ , γ_{LV} , γ_{SV} , and γ_{LS} are the surface tensions at the liquid–vapor, solid–vapor, and liquid–solid interfaces, respectively.

a planar composite electrolyte composed of $\beta''\text{-Al}_2\text{O}_3$ and YSZ (Yttria Stabilized Zirconia). The results indicate that improved stability was achieved at lower operating temperature due to limited particle growth of nickel and sodium chloride. Other issues that were deemed necessary for low temperature operation

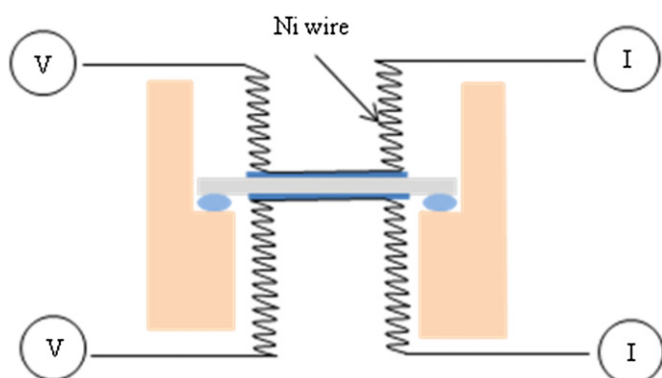


Fig. 3. Schematic for 4 pt electrical conductivity measurement.

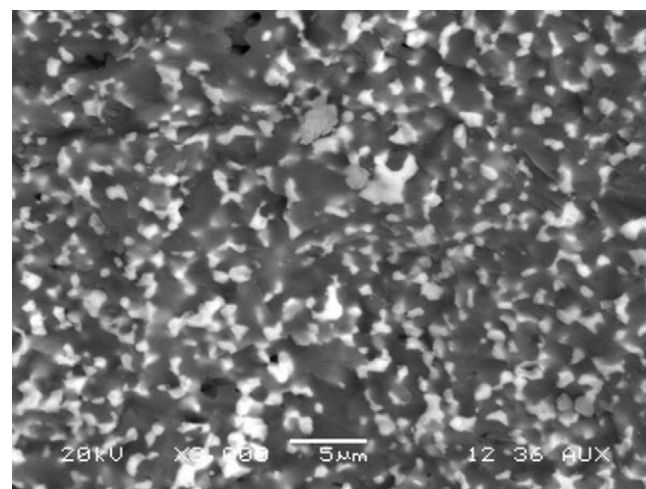


Fig. 4. Fracture surface of a $\beta''\text{-Al}_2\text{O}_3/\text{YSZ}$ composite sample.

include; lower resistance of the electrolyte and improved wetting of Na at low temperatures. These lower operating temperatures allow one to contemplate the use of polymeric seals. One of the issues preventing polymeric seals is that currently the sodium is applied above the service temperature for these polymers. Typically Na is applied at temperatures >300 °C. The lowering of the application temperature and the use of polymeric seals will dramatically lower the cost of implementation.

The wetting of $\beta''\text{-Al}_2\text{O}_3$ by liquid Na has received considerable attention because of the high local current densities in wet areas [5]. Areas of high current density can lead to the deterioration of the $\beta''\text{-Al}_2\text{O}_3$ under electrolytic conditions. Methods to improve wetting typically employ high temperatures (>300 °C) to facilitate wetting. The use of vacuum to remove absorbed surface moisture [6] and coatings (i.e. carbon and PbO) [7] to further facilitate wetting have also been proposed. However, in most cases the temperature at which good wetting occurs is above the use temperature of polymeric seals. This study will examine the possibility of initiating wetting of Na on $\beta''\text{-Al}_2\text{O}_3$ surfaces at low temperatures (≤ 200 °C).

Our premise in this experiment is “water interferes with the wetting of the beta alumina”. The alumina surface needs to be cleaned of all water and water reaction products. The clean alumina surface then needs to be protected by a material that is impervious

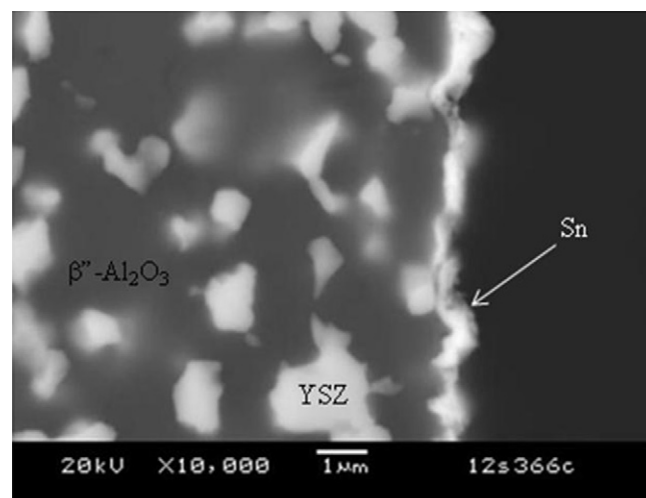


Fig. 5. Polished cross section of a sputtered Sn coating on the $\beta''\text{-Al}_2\text{O}_3/\text{YSZ}$ surface.

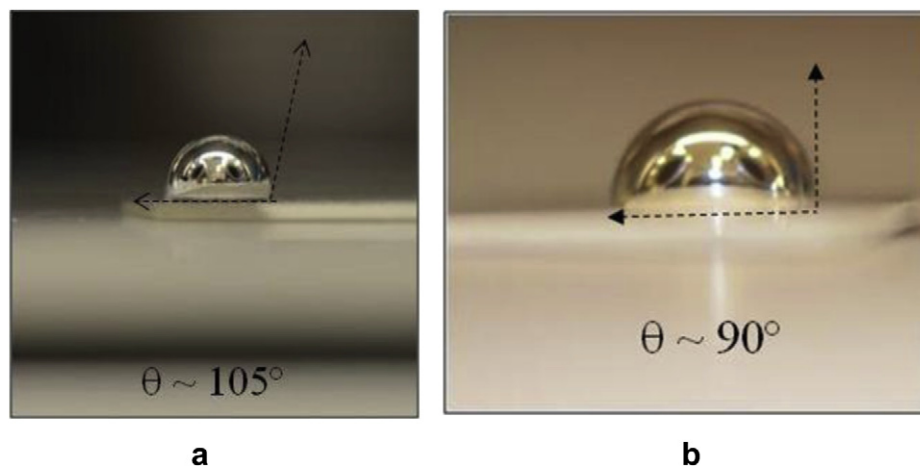


Fig. 6. Contact angle for the control sample at (a) 300 °C and (b) 350 °C.

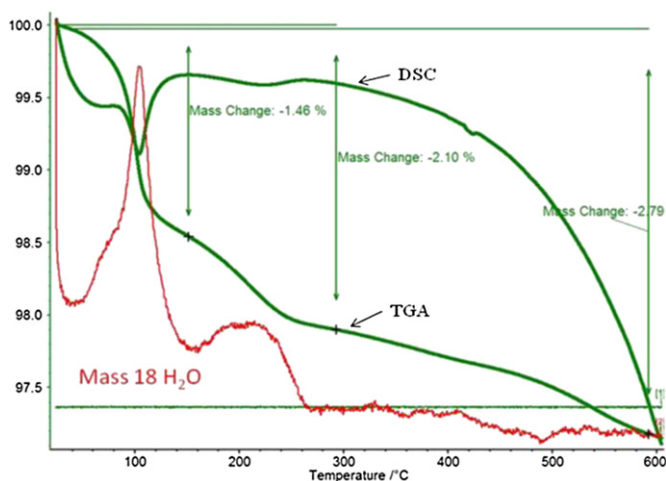


Fig. 7. TGA mass spec (H_2O) for a powdered $\beta''\text{-Al}_2\text{O}_3/\text{YSZ}$ sample.

to water yet will not interfere with the Na conductivity. The Na family of binary phase diagrams were scrutinized for a metal that could be applied, was non-reactive with water, and had complete miscibility with Na at low concentrations. The protecting metal layer would be $\approx 0.5 \mu\text{m}$ thick, and the Na layer is usually 1–2 mm

thick. Once dissolved in the sodium, the protecting metal would be less than 500 ppm, and the effect on conductivity should be minimal.

2. Experimental procedure

2.1. Fabrication of $\beta''\text{-Al}_2\text{O}_3/\text{YSZ}$ composite sheets

$\beta''\text{-Al}_2\text{O}_3/\text{YSZ}$ composite sheets were fabricated using the vapor phase process [8,9]. The starting powders were high purity $\alpha\text{-Al}_2\text{O}_3$ and YSZ. A mixture of 70 vol% $\alpha\text{-Al}_2\text{O}_3$ and 30 vol% YSZ was ball milled for 24 h to facilitate mixing, dried, and sieved. The powders were mixed with solvents and dispersants and further milled for 24 h. Plasticizers and binders were added into the slurry and further milled for 24 h. The slurry was de-aired and cast into thin sheets using a doctor blade. The sheets were allowed to dry for 24 h then laminated. The laminated sheets were then punched into circular sheets and fired in air at 1600 °C for 4 h to achieve a final fired density $>99\%$. Final sintered dimension were approximately 300 μm thick by 2.5 cm in diameter.

The fired sheets of $\alpha\text{-Al}_2\text{O}_3/\text{YSZ}$ composites were then fired at 1450 °C in a packed bed of $\beta''\text{-Al}_2\text{O}_3$ powder. The conversion of $\alpha\text{-Al}_2\text{O}_3$ to $\beta''\text{-Al}_2\text{O}_3$ occurs at high temperatures by the coupled transport of sodium and oxygen ions from the packed bed of $\beta''\text{-Al}_2\text{O}_3$ powders to the sintered sample. XRD was performed at this point. The $\alpha\text{-Al}_2\text{O}_3/\text{YSZ}$ sheets were found to be primarily YSZ and $\beta''\text{-Al}_2\text{O}_3$ with a very minor amount of $\beta\text{-Al}_2\text{O}_3$. The starting packing powder of $\beta''\text{-Al}_2\text{O}_3$ was synthesized using the solid state reaction of boehmite ($\text{Al}(\text{OH})_3$), Na_2CO_3 and Li_2CO_3 .

Composites sheets of $\beta''\text{-Al}_2\text{O}_3/\text{YSZ}$ were used for wetting and conductivity measurements. In addition, composites sheets were ground to a powder, exposed to air for different times and the water uptake was measured as a function of temperature using a TGA (thermogravimetric analyzer) mass spectrometer. Samples were heated at 3°C min^{-1} to 600 °C.

2.2. Preparation of $\beta''\text{-Al}_2\text{O}_3/\text{YSZ}$ composite surfaces

Sample preparation methods were employed to remove chemisorbed and physisorbed water on the composite surface and keep the surface clean prior to testing. Four different surface preparation techniques were used to study the wetting behavior of Na on $\beta''\text{-Al}_2\text{O}_3/\text{YSZ}$ surfaces and the conductivity of Na/ $\beta''\text{-Al}_2\text{O}_3/\text{YSZ}/\text{Na}$ cells, as listed in Table 1.

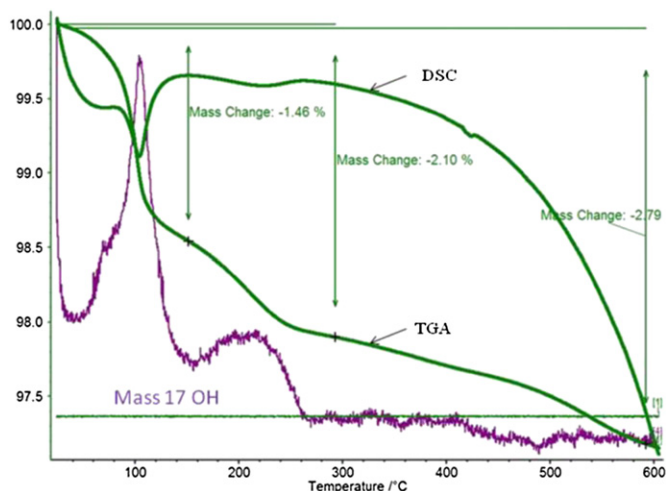


Fig. 8. TGA mass spec (OH) for a powdered $\beta''\text{-Al}_2\text{O}_3/\text{YSZ}$ sample.

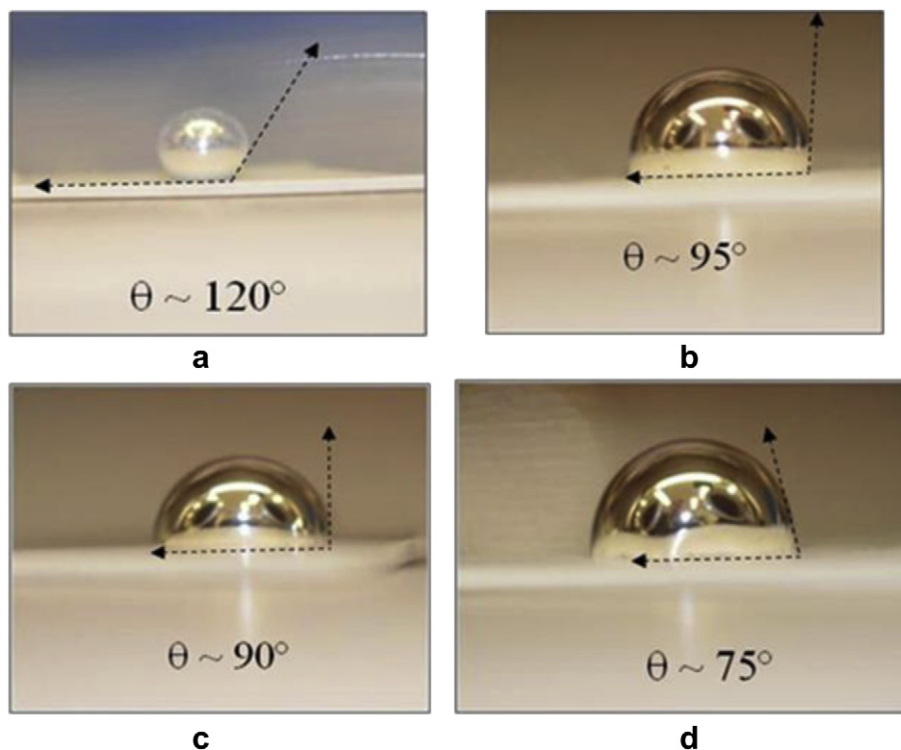


Fig. 9. Contact angle for samples prepared using Technique #2 at (a) 250 °C; (b) 300 °C; (c) 325 °C; and (d) 350 °C.

One surface of the composite sample was sputtered with Sn for wetting studies whereas both surface were masked and sputtered with Sn for conductivity measurements. Samples used in conductivity measurements were first glass sealed in alumina sample holders (Fig. 1) at 700 °C prior to surface preparation.

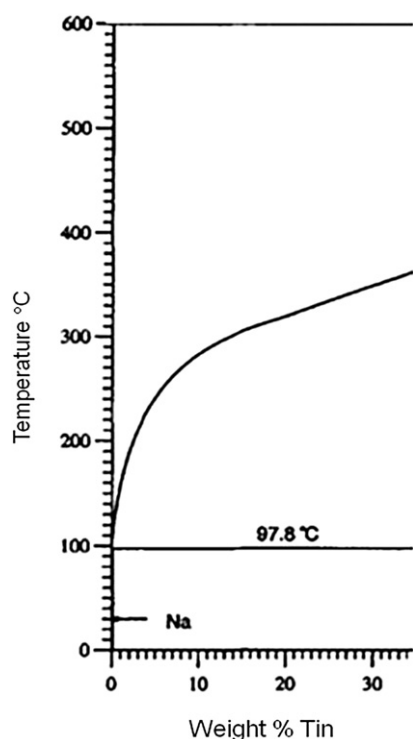


Fig. 10. Phase diagram of the Sn–Na system.

2.3. Sodium wetting on β'' -Al₂O₃/YSZ surfaces

The sessile drop technique was used to measure the contact angle of liquid sodium on β'' -Al₂O₃/YSZ surfaces. A schematic of a liquid drop on a solid surface is shown in Fig. 2. Wetting of the liquid on a solid surface means that the contact angle is zero or close to zero such that the liquid spreads over the surface easily, and nonwetting implies that the contact angle is greater than 90° such that the liquid balls up and can easily run off the surface [10]. Samples were heated on a hot plate in a glove box with low O₂ content (<5 ppm) and the temperature was measured using a thermocouple placed on the surface of the composite sheet. High purity Na was also heated to the testing temperature and drops of Na were transferred to the surface of the composite using a glass pipette. The sample surface was heated to temperatures between 150 °C and 350 °C.

2.4. Conductivity measurements of Na/ β'' -Al₂O₃/YSZ/Na cells

As described above, samples were glass sealed into Al₂O₃ sample holders and various surface preparation techniques were applied. Nickel wire was used as contacts for the 4-point conductivity measurement as shown in Fig. 3.

Sodium was then applied at 200 °C on one side, allowed to equilibrate, turned onto the second side, and Na was again applied and allowed to equilibrate. Electrical measurements were taken between 150 °C and 200 °C using a Solatron AC Impedance Analyzer and the frequency was swept from 1 Hz to 10 MHz with an applied signal of 10 mV.

3. Results and discussion

Sintered and converted composite samples of β'' -Al₂O₃/YSZ were fabricated to be ~300 μm thick by 2.5 cm in diameter, a typical microstructure of the bulk composite is shown in Fig. 4. In

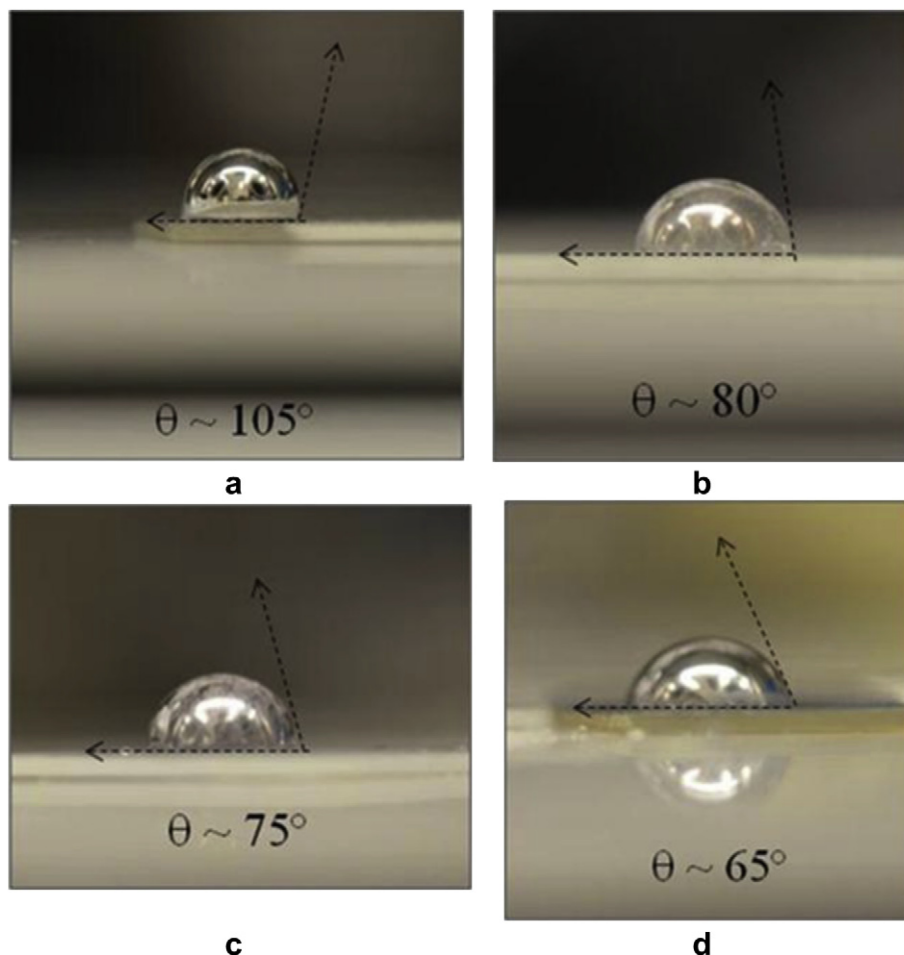


Fig. 11. Contact angle for samples prepared using Technique #3 at (a) 150 °C; (b) 200 °C; (c) 225 °C; and (d) 250 °C.

the SEM backscatter mode, the YSZ appears white and the β'' - Al_2O_3 appears dark. YSZ grains appear to be uniformly dispersed within the β'' - Al_2O_3 matrix.

Composite samples were then glassed into Al_2O_3 holders (for conductivity measurements) and exposed to various surface treatments, i.e. Sn sputtering. A typical cross section of the Sn coating is shown in Fig. 5. The Sn coating appears semi-uniform and approximately 0.5 μm in thickness.

3.1. Sessile drop experiments

Contact angles were found to have a large range depending on the surface preparation technique and the temperature of the composite surface. For the control sample (Technique #1) in which no attempt was made to remove any surface water, the ability of Na to wet the β'' - Al_2O_3 /YSZ surface was almost nonexistent. At very low temperature (≤ 200 °C), the Na drop would completely ball up and roll off the surface. This behavior was observed up ~ 300 °C. At temperature approaching 350 °C the Na would start to wet the composite surface and remain on the surface, Fig. 6.

TGA mass spectrometry suggests that the majority of the physisorbed and chemisorbed water has been removed slightly below 300 °C. TGA Mass spec runs for a composite sample that was ground into a powder and heated to 600 °C at 3 °C min^{-1} are shown in Figs. 7 and 8.

The mass spectra line for both H_2O and OH suggests that the majority of it is removed by 300 °C. The largest peak at 100 °C is

physisorbed water/hydroxyls and the smaller peak at ~ 200 °C and beyond is chemisorbed water/hydroxyls. Although the majority of weight loss occurs up to 300 °C, there is still a substantial amount of weight loss occurring above 300 °C. This is assumed to be contaminants (i.e. oils, foreign materials) picked up during the grinding process.

Contact angle measurements for technique #2 in which samples were heated to 300 °C in a deep vacuum showed improvement in the wetting behavior over the control sample. Shown in Fig. 9a–d, are contact angles for Na on composite sheets between 250 and 350 °C.

The contact angle decreases as the temperature increases. At temperatures below 250 °C, Na drops would not stay on the substrate but immediately rolled off. Although there was some improvement in heating the sample up in a deep vacuum before applying Na (Technique #2), a high temperature would still be needed (≥ 350) to facilitate wetting. This technique would not be a good option in fabricating low temperature Na beta batteries utilizing a seal with maximum operating condition at ~ 200 °C.

Therefore, alternative methods to facilitate Na wetting at low temperatures was investigated [11]. A method by which some material can protect the surface of the β'' - Al_2O_3 /YSZ composite (i.e. water uptake) but also induces wetting of the Na was employed. Ideally, the material would easily alloy with the Na and be present in small amounts that it would not be detrimental to the electrode reactions. Tin was chosen as a material to examine because it alloys with Na easily at low temperatures, see Fig. 10.

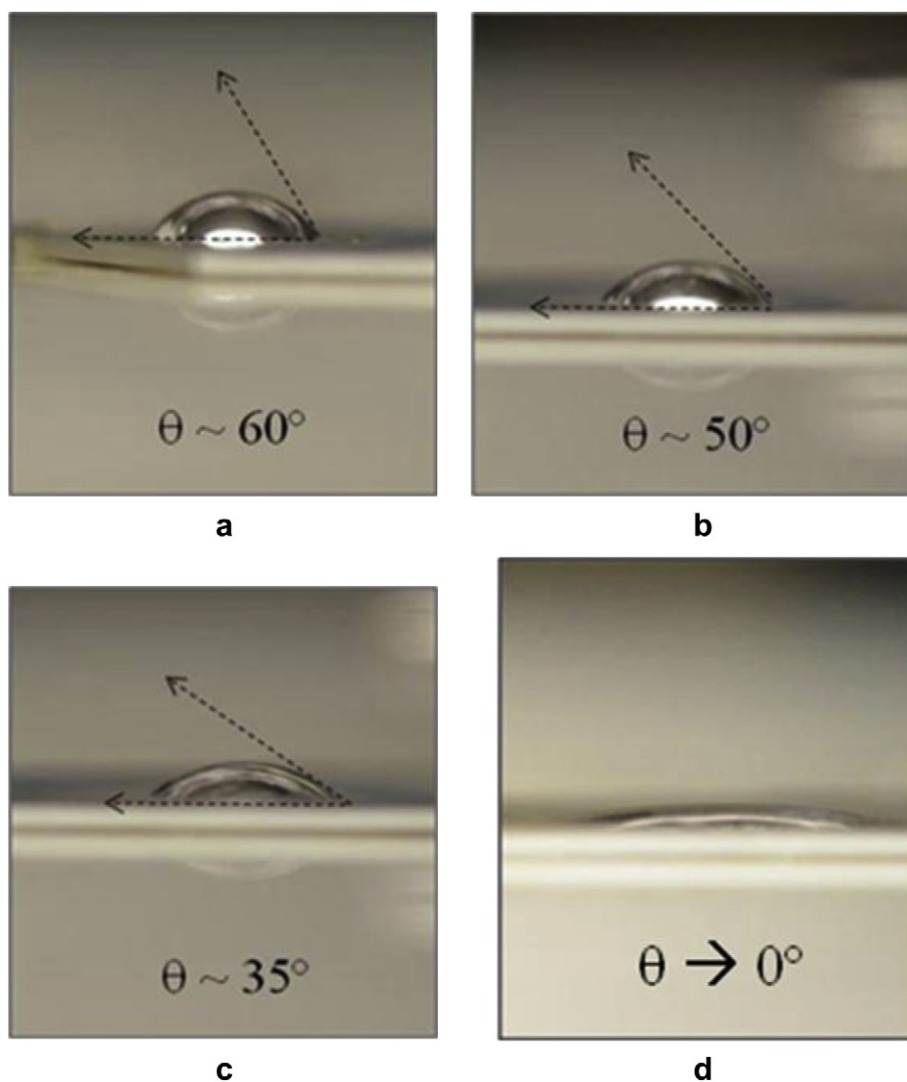


Fig. 12. Contact angle for samples prepared using Technique #4 at (a) 150 °C; (b) 200 °C; (c) 225 °C; and (d) 250 °C.

As shown in Fig. 10, at small Sn concentrations the material will melt at low temperatures and form predominately Na with a negligible amount of $\text{Na}_{15}\text{Sn}_4$. To minimize the amount of $\text{Na}_{15}\text{Sn}_4$, a sputtered film of $\sim 0.5 \mu\text{m}$ was used. This was found to be enough to minimize the overall amount of Sn but to cover the surface and limit the amount of water absorbed onto the surface. In general, the amount of Sn used is likely to be less than 0.3 wt% corresponding to 0.5 wt% $\text{Na}_{15}\text{Sn}_4$ and 99.5 wt% Na.

Technique # 3 was used to sputter a thin film of Sn at the surface and observe the contact angle as a function of temperature. Each temperature represents a new drop that is added at each temperature. The results from surface preparation technique # 3 are shown in Fig. 11a–d.

Use of Sn at the interface has dramatically improved the wetting at lower temperatures. Partial wetting, $<90^\circ$, is occurring at temperatures as low as 200 °C. The Na drop also tends to decrease

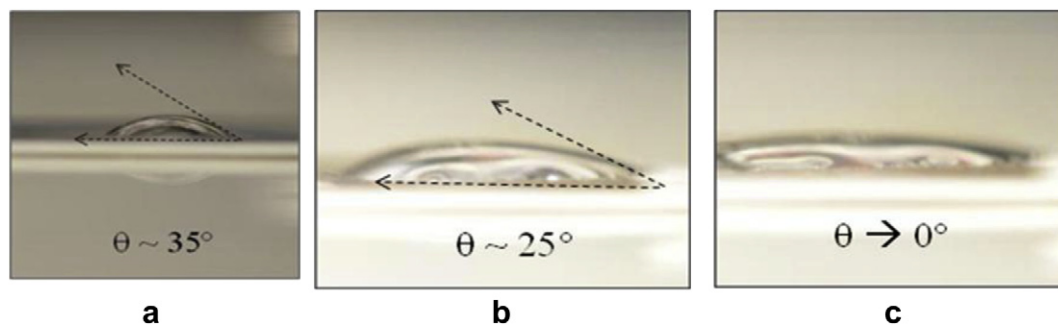


Fig. 13. Contact angle for samples prepared using Technique #4 at 225 °C for time (a) 0 min; (b) 2 min; and (c) 4 min.

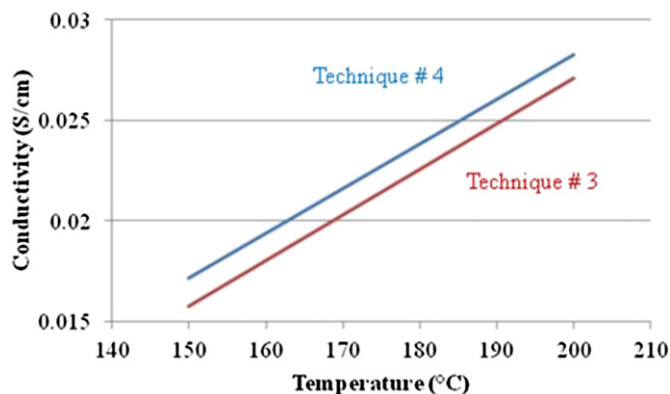


Fig. 14. Low temperature conductivity of samples with Sn coating at the interface.

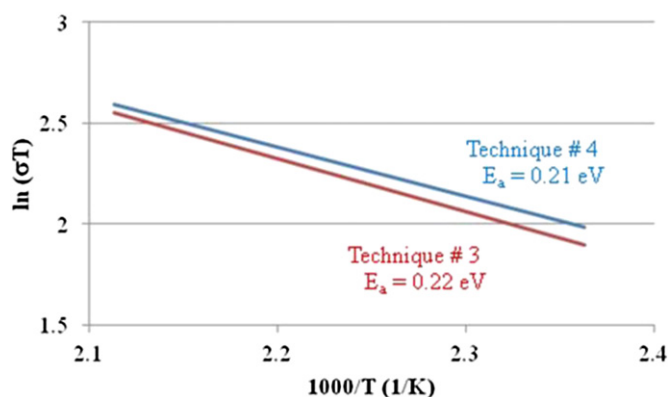


Fig. 15. Natural log versus $1000/T$ for surface preparation Techniques #3 and #4 between 150 °C and 200 °C.

with time at an isothermal hold, especially at higher temperatures. However, the Na is still not wetting at an optimum level that one would want to operate a cell at 200 °C. Technique # 4 was investigated in which the sample was first heat treated to 300 °C in a deep vacuum (10^{-6} atm) prior to sputtering. This additional step would first remove surface water before sputtering a thin Sn film. Again, sessile drop experiments were performed on these samples from 150 to 250 °C, the results are shown in Fig. 12a–d.

The use of Sn at the interface along with water removal before sputtering has again improved the wetting at lower temperatures. Good wetting has occurred at temperatures as low as 150 °C. Photos were taken immediately after the Na drop was applied to the surface. As stated earlier, the Na drop tends to decrease with time at an isothermal hold, Fig. 13.

Using Sn thin films as an intermediate layer to promote Na wetting on β'' - Al_2O_3 based substrates at low temperatures has the potential to allow low cost polymeric seals to be used in operating temperatures of ≤ 200 °C. Cleaning the surface prior to applying the Sn thin film is also important to minimize absorbed water that can hinder wetting.

3.2. Conductivity measurements

Sample resistance was measured using AC impedance spectroscopy and the conductivity was calculated from the sample dimensions. As shown in Fig. 3, the Ni contacts were applied to

a cell sealed in an Al_2O_3 holder and the Na was dropped onto one side at 200 °C. After the sample was allowed to equilibrate, the sample was turned over and Na was applied to the other side. Samples without Sn coatings were eliminated from conductivity measurements because the Na showed no adhesion to the β'' - Al_2O_3 /YSZ substrate. Therefore, conductivity as a function of temperature was limited to samples with Sn (Techniques #3 and #4), the results are shown in Figs. 14 and 15.

Conductivity of both samples prepared with Sn thin films at the interface fell within values reported in the literature. Pure β'' - Al_2O_3 has conductivity values of 0.1 S cm^{-1} at 200 °C [12]. Samples reported in this study are lowered than theoretical values most likely due to the 30% secondary phase of YSZ in the β'' - Al_2O_3 matrix. Activation energies of 0.21 eV and 0.22 eV also agree with values reported in the literature [13–15].

Conductivity values in agreement with values reported in the literature ensure uniform current densities within the β'' - Al_2O_3 based materials. Locally high current densities within the electrolyte caused by poor wetting could lead to deterioration of the β'' - Al_2O_3 material [5].

4. Conclusions

The use of thin films of Sn at the surface of β'' - Al_2O_3 samples was shown to improve the wetting of Na on the β'' - Al_2O_3 surface. A further improvement to the wetting behavior was accomplished by removing surface water at high temperature under vacuum prior to applying a thin film of Sn. Complete wetting on the β'' - Al_2O_3 /YSZ surface was achieved even at low temperature of 200 °C. Electrical conductivities and corresponding activation energies of samples with Sn thin films at the interface were in good agreement with values reported in the literature.

The use of Sn thin films as an intermediate layer to promote Na wetting on β'' - Al_2O_3 based substrates at low temperatures has the potential to allow low cost polymeric seals to be used at operating temperatures of ≤ 200 °C.

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